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(54) DESULFURIZING AGENT, METHOD FOR DESULFURIZATION AND METHOD FOR PRODUCING HYDROGEN FOR FUEL BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a desulfurizing agent which can effectively remove sulfur contents in a petroleum-based hydrocarbon and has a long life, to provide a desulfurization method by which the sulfur contents in the hydrocarbon oil can efficiently be removed down to a low concentration, and to provide a method for producing hydrogen for fuel batteries.

SOLUTION: This desulfurizing agent for petroleum-based hydrocarbons, is characterized by carrying at least one kind of basic functional groups on a carrier. The method for desulfurizing the petroleum-based hydrocarbon, is characterized by using the desulfurizing agent. The method for producing the hydrogen for fuel batteries, is characterized by bringing the petroleum-based hydrocarbon brought into contact with the desulfurizing agent into contact with a steam reformation catalyst.

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CLAIMS

[Claim(s)]

[Claim 1] The devulcanizing agent for petroleum system hydrocarbons which comes to support at least one sort of basic functional groups to support.

[Claim 2] The devulcanizing agent according to claim 1 whose support is porosity.

[Claim 3] The devulcanizing agent according to claim 1 or 2 whose support is the thing which is chosen from a silica, an alumina, a silica alumina, a zeolite, a titania, a zirconia, a magnesia, clay, clay, diatomaceous earth, activated carbon, and insoluble synthetic resin, and which consists of a kind at least.

[Claim 4] The devulcanizing agent according to claim 1 to 3 whose basic functional group is an amino group or the Pori amino group.

[Claim 5] The devulcanizing agent according to claim 1 to 4 which makes support carry out 0.1-10 milliequivalent support of the basic functional group per 1g of devulcanizing agents.

[Claim 6] The desulfurization approach of the petroleum system hydrocarbon characterized by desulfurizing using the devulcanizing agent for petroleum system hydrocarbons according to claim 1 to 5.

[Claim 7] The desulfurization approach according to claim 6 characterized by desulfurizing after processing a petroleum system hydrocarbon with an oxidizer beforehand.

[Claim 8] The desulfurization approach according to claim 7 by which an oxidizer is chosen from the alkali salt and ozone of the alkali salt of a hydrogen peroxide, a peroxy acid, a metal peroxide, and a metal peroxide, a hypochlorous-acid ghost, a chloric-acid ghost, a hypochlorous-acid ghost, or a chloric-acid ghost and which is a kind at least.

[Claim 9] - The desulfurization approach according to claim 6 to 8 of contacting a petroleum system hydrocarbon to a devulcanizing agent in the temperature of 40-100 degrees C.

[Claim 10] The desulfurization approach of the petroleum system hydrocarbon characterized by making the second devulcanizing agent contact after carrying out desulfurization processing of the petroleum system hydrocarbon by the desulfurization approach according to claim 6 to 9.

[Claim 11] The desulfurization approach according to claim 10 which is that in which the second devulcanizing agent contains at least a kind of metal chosen from nickel, Cr, Mn, Fe, Co, Cu, Zn, Pd, Ir, and Pt.

[Claim 12] The manufacture approach of the hydrogen for fuel cells characterized by making a steam-reforming catalyst contact after carrying out desulfurization processing of the petroleum system hydrocarbon by the desulfurization approach according to claim 6 to 11.

[Claim 13] The manufacture approach of the hydrogen for fuel cells according to claim 12 that a steam-reforming catalyst is a ruthenium system catalyst.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the devulcanizing agent of a petroleum system hydrocarbon, the desulfurization approach, and the manufacture approach of the hydrogen for fuel cells. This invention removes the sulfur content in a petroleum system hydrocarbon for the sulfur content in a petroleum system hydrocarbon efficiently to low concentration removable using the long devulcanizing agent of a life, and this devulcanizing agent effectively, carries out steam-reforming processing of the desulfurization approach that long duration may be made to carry out rear-spring-supporter maintenance of the engine performance of the reforming catalyst in the steam-reforming part which is a down-stream facility, and the petroleum system hydrocarbon processed by this desulfurization approach, and relates to the approach of manufacture the hydrogen for fuel cells, in more detail.

[0002]

[Description of the Prior Art] In recent years, the new energy technique is in the limelight from the environmental problem, and the fuel cell attracts attention as one of the new energy technique of this. When this fuel cell makes hydrogen and oxygen react electrochemically, chemical energy is transformed into electrical energy, it has the description that the utilization effectiveness of energy is high, and utilization research is positively made as a noncommercial use, industrial use, or an object for automobiles. According to the class of electrolyte used for this fuel cell, the type of a phosphoric-acid mold, a melting carbonate mold, a solid acid ghost mold, a solid-state macromolecule mold, etc. is known. The activity of hydrocarbons, such as LPG of a petroleum system, naphtha, and kerosene, is studied by the town gas which, on the other hand, uses as a principal component the liquefied natural gas which makes a methanol and methane a subject, and this natural gas as a source of hydrogen, the synthetic liquid fuel which uses natural gas as a raw material, and the pan. When using a fuel cell for a noncommercial use or automobiles, since the distribution system is fixed, a gas station, a dealer, etc. are advantageous [the above-mentioned petroleum system hydrocarbon] as sources of hydrogen the top where storage and handling are easy.

[0003] However, a petroleum system hydrocarbon has the problem that there are many contents of sulfur content, compared with the thing of a methanol or a natural gas system. When manufacturing hydrogen using this petroleum system hydrocarbon, generally steam reforming or the approach of carrying out partial oxidation refining processing is used for the bottom of existence of a reforming catalyst in this hydrocarbon. In such refining processing, in order to carry out poisoning of the above-mentioned reforming catalyst by the sulfur content in a hydrocarbon, it is important to perform desulfurization processing to this hydrocarbon and to usually make a sulfur content content below into the 0.2 weight ppm from the point of a catalyst life. The approach which research of the former many is made, for example, is hydrodesulfurized at the temperature of 200-400 degrees C under the pressure of ordinary pressure -5MPa as the desulfurization approach of a petroleum system hydrocarbon using hydrogen-sulfide adsorbents, such as hydrodesulfurization catalysts, such as Co-Mo/alumina, and nickel-Mo/alumina, and ZnO, is learned. This approach performs hydrodesulfurization under severe conditions, it is the

approach of using sulfur content as a hydrogen sulfide and removing it and since it is difficult, making sulfur content below into the 0.2 weight ppm moreover cannot apply it to the hydrocarbon for fuel cells easily.

[0004] Moreover, in order to learn the method (JP,4-72387,A) of oxidizing with an oxidizer and removing a sulfur compound as the desulfurization approach of a petroleum fraction using lifting of the melting point or the boiling point and to promote the reaction of a sulfur compound and an oxidizer, how to introduce an oxidation catalyst is also learned (JP,11-140462,A). However, when these approaches are applied to desulfurization of petroleum system hydrocarbons, such as kerosene, since sulfur concentration is a minute amount, sufficient separation recovery cannot be attained, and the actual condition has not resulted in practical level as a devulcanizing agent for fuel cells.

[0005]

[Problem(s) to be Solved by the Invention] The 1st object of this invention is under such a situation to be able to remove the sulfur content in a petroleum system hydrocarbon effectively, and offer the long devulcanizing agent of a life. Moreover, using this devulcanizing agent, the 2nd object of this invention removes the sulfur content in a petroleum system hydrocarbon efficiently to low concentration, and is to offer the desulfurization approach that long duration may be made to carry out rear-spring-supporter maintenance of the engine performance of the reforming catalyst in the steam-reforming part which is a down-stream facility. Furthermore, the 3rd object of this invention is to offer the approach of manufacturing the hydrogen for fuel cells efficiently, using the petroleum system hydrocarbon processed by the above-mentioned desulfurization approach.

[0006]

[Means for Solving the Problem] this invention persons analyzed in the detail about the description of the sulfur compound in a petroleum system hydrocarbon first, in order to attain said object. Consequently, as a sulfur compound contained in a petroleum system hydrocarbon, benzothiophene or dibenzo thiophenes are dominant in the point of the desulfurization engine performance, and the adsorption to the devulcanizing agent of these sulfur compounds found out the important thing in respect of improvement in the desulfurization engine performance. And generally it is known that such benzothiophene and dibenzo thiophenes will oxidize to a sulfoxide compound or a sulfone compound with various oxidizers. this invention persons by adsorbing a sulfoxide compound or a sulfone compound using the sulfoxide compound or sulfone compound by which generation was carried out [above-mentioned], and the devulcanizing agent which contains reactant strongly paying attention to the above-mentioned point That benzothiophene and dibenzo thiophenes are removable as a result A header, Wholeheartedly, the devulcanizing agent which comes to support a specific radical to the result of research, especially support could carry out adsorption treatment of benzothiophene and the dibenzo thiophenes selectively, and found out that said 1st object might be suited as a devulcanizing agent for petroleum system hydrocarbons.

[0007] Moreover, it found out that said 2nd object could be attained by carrying out desulfurization processing of the petroleum system hydrocarbon, and making the second devulcanizing agent contact by the case further using the above-mentioned devulcanizing agent. Furthermore, in the above-mentioned desulfurization approach, it found out that said 3rd object could be attained by contacting the petroleum system hydrocarbon after making a devulcanizing agent contact for a steam-reforming catalyst. This invention is completed based on this knowledge. That is, after carrying out desulfurization processing of the petroleum system hydrocarbon by the desulfurization approach of the petroleum system hydrocarbon characterized by for this invention to desulfurize to (1) support using the devulcanizing agent for petroleum system hydrocarbons and the (2) above-mentioned devulcanizing agent which come to support a basic functional group, and the approach of (3) above (2), the manufacture approach of the hydrogen for fuel cells characterized by to make a steam-reforming catalyst contact offers.

[0008]

[Embodiment of the Invention] First, the devulcanizing agent of this invention is explained. The devulcanizing agent of this invention makes support support a basic functional group. As this

support, a porous thing is desirable. As such porosity support, a porous inorganic oxide, for example, a silica, an alumina, a silica alumina, a zeolite, a titania, a zirconia, a magnesia, a zinc oxide, clay, diatomaceous earth, activated carbon, insoluble synthetic resin, etc. can be mentioned preferably. Although such porosity support may be used independently and you may use combining two or more sorts, in these, insoluble synthetic resin is especially suitable. As insoluble synthetic resin, the synthetic resin which copolymerized and obtained the styrene monomer and the divinylbenzene, the synthetic resin which condensed the meta-phenylenediamine with formaldehyde and obtained it can be used, for example.

[0009] As a basic functional group which such support is made to support, the amino group or the Pori amino group is desirable. Since these functional groups have the strong polarity, the quality of acidity and a strong polar sulfoxide, or a sulfone is adsorbed easily. As an approach of supporting such a basic functional group to support, the approach by gas adsorption, the approach by the installation from a water solution, the approach by the polymerization reaction of the monomer containing the above-mentioned functional group, etc. are mentioned. Under existence of the gas which contains the amino compound or the Pori amino compounds, such as ammonia and a hydrazine hydrate, as an approach by gas adsorption, for example, There is an approach to which this compound and support are made to react, and as an approach by the installation from a water solution There is an approach by the approach of well-known arbitration, such as an impregnation method using the solution containing the amino compound or the Pori amino compounds, such as ammonia, a hydrazine, a urea, an aniline, and amino alcohol, a coprecipitation method, a method of kneading support gel, and an ion-exchange method. Moreover, the approach of making amines react to what carried out chromium methylation of the copolymer as an approach by the polymerization reaction of the monomer containing the above-mentioned functional group etc. is mentioned.

[0010] The amount of support to the support of the above-mentioned basic functional group has the desirable range per 1g of support, and of 0.1 – 10 milliequivalent. If there is a possibility that the desulfurization engine performance may not fully be demonstrated for this amount of support at less than 0.1 % of the weight and it, on the other hand, exceeds 10 % of the weight, the structure on the support of a basic functional group changes, and it is not desirable. The more desirable amount of support of the field of the desulfurization engine performance to this basic functional group is the range per 1g of support, and of 0.2 – 5 milliequivalent. Moreover, there is especially no limit as a configuration of a devulcanizing agent, for example, the shape of the shape of the letter of grinding, a pellet type, and a tablet and a bead etc. can be mentioned. As a petroleum system hydrocarbon with which the devulcanizing agent of this invention is applied, although LPG, a gasoline, naphtha, kerosene, gas oil, etc. are mentioned for example, the petroleum system hydrocarbon which has the boiling point below kerosene in these is desirable. If it is in kerosene, it is desirable that a sulfur content content applies to the JIS No. 1 kerosene below the 80 weight ppm.

[0011] Next, the desulfurization approach of this invention is explained. After carrying out desulfurization processing of the petroleum system hydrocarbon using the devulcanizing agent of this invention of (1) above-mentioned by the approach (the desulfurization approach I of this invention is called hereafter.) of carrying out desulfurization processing of the petroleum system hydrocarbon, and the (2) above-mentioned desulfurization approach I, there are two modes of an approach (the desulfurization approach II of this invention is called hereafter.) contacted to the second devulcanizing agent in the desulfurization approach of this invention. In the desulfurization approach I of this invention, a petroleum system hydrocarbon can be put into containers, such as an approach of circulating a petroleum system hydrocarbon to a devulcanizing agent, and a tank which fixed the devulcanizing agent to the interior, as a desulfurization format, and standing or the approach of agitating can be mentioned preferably. Moreover, the temperature to which this devulcanizing agent and a petroleum system hydrocarbon are contacted in this case has the desirable range of -40-100 degrees C. Since the adsorption engine performance of a devulcanizing agent will fall if this temperature exceeds 100 degrees C preferably, since the fluidity of this hydrocarbon falls below -40 degrees C, it is not desirable. In addition, a pressure is usually ordinary pressure -1MPa in this case.

[0012] In the above-mentioned desulfurization approach, it is desirable to use the petroleum system hydrocarbon beforehand processed with the oxidizer as a raw material petroleum system hydrocarbon. By such processing, the thiophenes contained in a petroleum system hydrocarbon can oxidize to a sulfoxide compound or a sulfone compound, and the desulfurization engine performance can be made to improve by using the devulcanizing agent of this invention further. As an oxidizer which can be used in this invention, although there is especially no limit, the alkali salt of the alkali salt of a hydrogen peroxide, a peroxy acid, a metal peroxide, and a metal peroxide, a hypochlorous-acid ghost, a chloric-acid ghost, a hypochlorous-acid ghost, or a chloric-acid ghost, ozone, etc. are mentioned preferably. Two or more sorts can be combined and the above-mentioned oxidizer can also be used, although you may use independently. For oxidizing to a sulfoxide compound or a sulfone compound as amount of the oxidizer used in all the sulfur compounds that are contained in a petroleum system hydrocarbon and that should oxidize, although what is necessary is just more than a complement, it is desirable to usually add 2-8 oxygen atoms per sulfur atom and the oxidizer of the amount which supplies 3-4 oxygen atoms especially, when oxidizing a sulfur compound to a sulfoxide compound or a sulfone compound promptly. Moreover, as for an oxidizer, it is desirable to dissolve and use the handling nature for a petroleum system hydrocarbon and the dissolving solvent from the point made easy.

[0013] In the desulfurization approach II of this invention, after being the above [a petroleum system hydrocarbon], making, using the devulcanizing agent of above-mentioned this invention as the first devulcanizing agent and carrying out desulfurization processing, adsorption desulfurization of this hydrocarbon can be efficiently performed by making the second devulcanizing agent contact. As the second devulcanizing agent of the above, there is especially no limit, it may use another adsorption devulcanizing agent, and may use hydrodesulfurization catalysts, such as Co-Mo/alumina, and a nickel-Mo alumina. As another former adsorption devulcanizing agent, the thing which is chosen, for example from Cr, Mn, Fe, Co, nickel, Cu, Zn, Pd, Ir, and Pt and which supported a kind to porosity support is desirable at least. What supported especially nickel to porosity support is suitable. As for the amount of support of these metal components, it is desirable that it is 30 - 80 % of the weight based on points, such as desulfurization engine performance, to the devulcanizing-agent whole quantity. These adsorption devulcanizing agents can raise the desulfurization engine performance by carrying out hydrogen reduction beforehand. Moreover, in using the latter hydrodesulfurization catalyst, in case it contacts a petroleum system hydrocarbon for this hydrodesulfurization catalyst as the second devulcanizing agent, a small amount of hydrogen may be added.

[0014] It is desirable to contact directly the petroleum system hydrocarbon in which desulfurization processing was carried out by the devulcanizing agent of this invention to the second devulcanizing agent as the desulfurization approach by this second devulcanizing agent. Moreover, beforehand, desulfurization processing is carried out by the devulcanizing agent of this invention, and a petroleum system hydrocarbon may be contacted to the second devulcanizing agent in somewhere else at reaction time. As a reaction condition at the time of making the second devulcanizing agent contact, a petroleum system hydrocarbon can be suitably selected according to the class of the second devulcanizing agent to be used. For example, when a nickel system adsorption devulcanizing agent is used as the second devulcanizing agent and kerosene is used as a petroleum system hydrocarbon, the range of contact temperature is usually 130-230 degrees C, and a pressure is usually ordinary pressure - 1 MPa-G extent. In the desulfurization approach II of such this invention, it is possible by choosing desulfurization conditions suitably to make sulfur content in a petroleum system hydrocarbon below into the 0.2 weight ppm.

[0015] Next, the manufacture approach of the hydrogen for fuel cells of this invention is explained. In this approach, the hydrogen for fuel cells is manufactured by contacting the petroleum system hydrocarbon by which desulfurization processing was carried out in the desulfurization approach of said this invention for a steam-reforming catalyst. As a steam-reforming catalyst used in the approach of this invention, there is especially no limit, out of the well-known thing conventionally known as a steam-reforming catalyst of a hydrocarbon, can choose the thing of arbitration suitably and can use it. As such a steam-reforming catalyst, what

supported noble metals, such as nickel, a zirconium, etc. As mentioned, for example, suitable support. Kind support may be carried out and the above-mentioned support metal may be made to support combining two or more sorts. In these catalysts, the thing (a ruthenium system catalyst is called hereafter.) which made the ruthenium support is desirable, and the effectiveness which controls the carbon deposit under steam-reforming reaction is large. In the case of this ruthenium system catalyst, the amount of support of a ruthenium has 0.05 – 20% of the weight of the desirable range on support criteria, and it is 0.1 – 2% of the weight of the range especially preferably 0.05 to 15% of the weight more preferably.

[0016] When supporting this ruthenium, it can support by request combining other metals. As these other metals, a zirconium, cobalt, magnesium, etc. are mentioned, for example. On the other hand, as support, an inorganic oxide is desirable and an alumina, a silica, a zirconia, magnesias, such mixture, etc. are specifically mentioned. In these, especially an alumina and a zirconia are suitable. a ratio with the carbon which originates in a steam and a petroleum system hydrocarbon as a reaction condition in steam-reforming processing — S/C (mole ratio) — usually — 2-5 — desirable — 2-4 — it is more preferably selected in 2-3. When there is a possibility that the amount of generation of hydrogen may fall [a S/C mole ratio] less than by two and 5 is exceeded, a superfluous steam is needed, a heat loss is large, and since the effectiveness of hydrogen manufacture falls, it is not desirable.

[0017] Moreover, it is desirable to keep the inlet temperature of a steam-reforming catalyst bed at 630 degrees C or less and 600 more degrees C or less, and to perform steam reforming. If inlet temperature exceeds 630 degrees C, the pyrolysis of a hydrocarbon may be promoted, carbon may deposit in a catalyst or a reaction tube wall, and operation may become difficult. In addition, although especially a limit does not have catalyst bed outlet temperature, the range of 650-800 degrees C is desirable. If catalyst bed outlet temperature has fear which is not enough and exceeds 800 degrees C, a reactor may need heat-resisting material and is not economically desirable. reaction pressure — usually — ordinary pressure -3MPa — desirable — the range of ordinary pressure -1MPa — it is — moreover, LHSV — usually — 0.1-100h⁻¹ — it is the range of 0.2-50h⁻¹ preferably. Thus, the hydrogen for fuel cells can be manufactured efficiently.

[0018]

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples. In addition, the kerosene used for the desulfurization trial is the JIS No. 1 kerosene of the sulfur content 65 weight ppm. In addition, the distillation curve of the JIS No. 1 kerosene to be used is as follows.

initial boiling point :152-degree-C10% distillation-temperature: -- 169-degree-C30% distillation-temperature: -- 184-degree-C50% distillation-temperature: -- 203-degree-C70% distillation-temperature: -- 224-degree-C90% distillation-temperature: -- 254-degree-C terminal point : 276 degrees C [0019] Copolymerize the preparation styrene monomer and divinylbenzene of an example 1 (1) devulcanizing agent, prepare giant-molecule support (weight average molecular weight 106, a styrene:divinylbenzene ratio: 10:1), and made this giant-molecule support and 90 degrees C of chloro methyl ether react for 2 hours, and added the trimethylamine further, it was made to react at a room temperature for 8 hours, and the devulcanizing agent was obtained. The amount of support of the Pori amino group was 3 milliequivalent per 1g of macromolecule support.

[0020] (2) 2.5l. of desulfurization trial ** JIS No. 1 kerosene was held in the container with a capacity of 5l., 250ml (30%) of hydrogen peroxide solution was added to this, and it stirred at the room temperature for 3 hours. Separation recovery of the part for kerosene was carried out after stirring termination. The sulfur concentration after the recovery obtained by this trial was 50 ppm. After holding 2l. of kerosene obtained by the above-mentioned processing, and 500g of devulcanizing agents obtained by the above (1) in the container with a capacity of 5l. and agitating them at a room temperature for 24 hours, separation recovery of the part for kerosene was carried out. The sulfur content concentration in the collected kerosene was the amount ppm of duplexs.

** As the second devulcanizing agent, after calcinating 15ml (70 % of the weight the amount of

nickel support : as metal (nickel) of nickel support diatomaceous earth at 400 degrees C, the coil made from stainless steel with a bore of 17mm was filled up. Subsequently, after carrying out temperature up to 120 degrees C in the bottom hydrogen air current of ordinary pressure and holding for 1 hour, temperature up was carried out further, it held at 380 degrees C for 1 hour, and the nickel support diatomaceous earth devulcanizing agent was activated. Then, it held at 150 degrees C. Next, the desulfurization kerosene obtained by the aforementioned ** was circulated to the coil in liquid-hourly-space-velocity (LHSV) 10h⁻¹ under ordinary pressure, and the sulfur content concentration in the processing kerosene after 5-hour progress was analyzed. Consequently, sulfur content concentration was below the 0.2 weight ppm.

[0021] The acquired catalyst was dried and the devulcanizing agent was obtained, after adding 680ml of aqueous ammonia 1% to 100g of preparation activated carbon of an example 2 (1) devulcanizing agent. The amount of support of the amino group was 4 milliequivalent per 1g of activated carbon.

(2) When the desulfurization trial was carried out like the example 1 (2) using the devulcanizing agent obtained by the desulfurization test above (1), the sulfur content concentration in the kerosene after 5-hour progress was below the 0.2 weight ppm.

[0022] 250ml (30%) of hydrogen peroxide solution, 50ml of formic acid, and 250ml of acetones were added to 2.5l. of same JIS No. 1 kerosene with having used in the example 1 (1) example 1 of a comparison, and 3-hour stirring and a reaction were performed at 40 degrees C. The sodium sulfite water solution of 2 conventions of reaction mixture washes after a reaction, an organic phase is further dried after washing with distilled water, it distills with a precision distillation apparatus, and the fraction of 220-350 degrees C of boiling points is taken. The sulfur content concentration in purification kerosene was 5 % of the weight.

(2) When the desulfurization trial was carried out like example 1 (2) ** using the kerosene obtained by the above (1), the sulfur content concentration in the kerosene after 5-hour progress was the 0.5 weight ppm.

[0023] The kerosene obtained in (1) of the example 1 of example of comparison 2 comparison was diluted with Deccan which does not contain sulfur further, and the sulfur concentration was made into the amount ppm of duplexes. When the desulfurization trial was carried out like example 1 (2) ** using the kerosene diluted with above-mentioned Deccan, the sulfur content concentration in the kerosene after 5-hour progress was the 1.0 weight ppm.

[0024]

[Effect of the Invention] Its life is long while the devulcanizing agent of this invention can remove effectively the sulfur content in a petroleum system hydrocarbon, especially kerosene. Moreover, according to the desulfurization approach of this invention, the sulfur content in a petroleum system hydrocarbon can be efficiently removed to low concentration, and a long time can be made to carry out rear-spring-supporter maintenance of the engine performance of the reforming catalyst in the steam-reforming part which is a down-stream facility. Moreover, the hydrogen for fuel cells can be efficiently manufactured by carrying out steam-reforming processing of the petroleum system hydrocarbon processed by this desulfurization approach.

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TECHNICAL FIELD

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the devulcanizing agent of a petroleum system hydrocarbon, the desulfurization approach, and the manufacture approach of the hydrogen for fuel cells. This invention removes the sulfur content in a petroleum system hydrocarbon for the sulfur content in a petroleum system hydrocarbon efficiently to low concentration removable using the long devulcanizing agent of a life, and this devulcanizing agent effectively, carries out steam-reforming processing of the desulfurization approach that long duration may be made to carry out rear-spring-supporter maintenance of the engine performance of the reforming catalyst in the steam-reforming part which is a down-stream facility, and the petroleum system hydrocarbon processed by this desulfurization approach, and relates to the approach of manufacture the hydrogen for fuel cells, in more detail.

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PRIOR ART

[Description of the Prior Art] In recent years, the new energy technique is in the limelight from the environmental problem, and the fuel cell attracts attention as one of the new energy technique of this. When this fuel cell makes hydrogen and oxygen react electrochemically, chemical energy is transformed into electrical energy, it has the description that the utilization effectiveness of energy is high, and utilization research is positively made as a noncommercial use, industrial use, or an object for automobiles. According to the class of electrolyte used for this fuel cell, the type of a phosphoric-acid mold, a melting carbonate mold, a solid acid ghost mold, a solid-state macromolecule mold, etc. is known. The activity of hydrocarbons, such as LPG of a petroleum system, naphtha, and kerosene, is studied by the town gas which, on the other hand, uses as a principal component the liquefied natural gas which makes a methanol and methane a subject, and this natural gas as a source of hydrogen, the synthetic liquid fuel which uses natural gas as a raw material, and the pan. When using a fuel cell for a noncommercial use or automobiles, since the distribution system is fixed, a gas station, a dealer, etc. are advantageous [the above-mentioned petroleum system hydrocarbon] as sources of hydrogen the top where storage and handling are easy.

[0003] However, a petroleum system hydrocarbon has the problem that there are many contents of sulfur content, compared with the thing of a methanol or a natural gas system. When manufacturing hydrogen using this petroleum system hydrocarbon, generally steam reforming or the approach of carrying out partial oxidation refining processing is used for the bottom of existence of a reforming catalyst in this hydrocarbon. In such refining processing, in order to carry out poisoning of the above-mentioned reforming catalyst by the sulfur content in a hydrocarbon, it is important to perform desulfurization processing to this hydrocarbon and to usually make a sulfur content content below into the 0.2 weight ppm from the point of a catalyst life. The approach which research of the former many is made, for example, is hydrodesulfurized at the temperature of 200-400 degrees C under the pressure of ordinary pressure -5MPa as the desulfurization approach of a petroleum system hydrocarbon using hydrogen-sulfide adsorbents, such as hydrodesulfurization catalysts, such as Co-Mo/alumina, and nickel-Mo/alumina, and ZnO, is learned. This approach performs hydrodesulfurization under severe conditions, it is the approach of using sulfur content as a hydrogen sulfide and removing it, and since it is difficult, making sulfur content below into the 0.2 weight ppm moreover cannot apply it to the hydrocarbon for fuel cells easily.

[0004] Moreover, in order to learn the method (JP,4-72387,A) of oxidizing with an oxidizer and removing a sulfur compound as the desulfurization approach of a petroleum fraction using lifting of the melting point or the boiling point and to promote the reaction of a sulfur compound and an oxidizer, how to introduce an oxidation catalyst is also learned (JP,11-140462,A). However, when these approaches are applied to desulfurization of petroleum system hydrocarbons, such as kerosene, since sulfur concentration is a minute amount, sufficient separation recovery cannot be attained, and the actual condition has not resulted in practical level as a devulcanizing agent for fuel cells.

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EFFECT OF THE INVENTION

[Effect of the Invention] Its life is long while the devulcanizing agent of this invention can remove effectively the sulfur content in a petroleum system hydrocarbon, especially kerosene. Moreover, according to the desulfurization approach of this invention, the sulfur content in a petroleum system hydrocarbon can be efficiently removed to low concentration, and a long time can be made to carry out rear-spring-supporter maintenance of the engine performance of the reforming catalyst in the steam-reforming part which is a down-stream facility. Moreover, the hydrogen for fuel cells can be efficiently manufactured by carrying out steam-reforming processing of the petroleum system hydrocarbon processed by this desulfurization approach.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The 1st object of this invention is under such a situation to be able to remove the sulfur content in a petroleum system hydrocarbon effectively, and offer the long devulcanizing agent of a life. Moreover, using this devulcanizing agent, the 2nd object of this invention removes the sulfur content in a petroleum system hydrocarbon efficiently to low concentration, and is to offer the desulfurization approach that long duration may be made to carry out rear-spring-supporter maintenance of the engine performance of the reforming catalyst in the steam-reforming part which is a down-stream facility. Furthermore, the 3rd object of this invention is to offer the approach of manufacturing the hydrogen for fuel cells efficiently, using the petroleum system hydrocarbon processed by the above-mentioned desulfurization approach.

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MEANS

[Means for Solving the Problem] this invention persons analyzed in the detail about the description of the sulfur compound in a petroleum system hydrocarbon first, in order to attain said object. Consequently, as a sulfur compound contained in a petroleum system hydrocarbon, benzothiophene or dibenzo thiophenes are dominant in the point of the desulfurization engine performance, and the adsorption to the devulcanizing agent of these sulfur compounds found out the important thing in respect of improvement in the desulfurization engine performance. And generally it is known that such benzothiophene and dibenzo thiophenes will oxidize to a sulfoxide compound or a sulfone compound with various oxidizers. this invention persons by adsorbing a sulfoxide compound or a sulfone compound using the sulfoxide compound or sulfone compound by which generation was carried out [above-mentioned], and the devulcanizing agent which contains reactant strongly paying attention to the above-mentioned point That benzothiophene and dibenzo thiophenes are removable as a result A header, Wholeheartedly, the devulcanizing agent which comes to support a specific radical to the result of research, especially support could carry out adsorption treatment of benzothiophene and the dibenzo thiophenes selectively, and found out that said 1st object might be suited as a devulcanizing agent for petroleum system hydrocarbons.

[0007] Moreover, it found out that said 2nd object could be attained by carrying out desulfurization processing of the petroleum system hydrocarbon, and making the second devulcanizing agent contact by the case further using the above-mentioned devulcanizing agent. Furthermore, in the above-mentioned desulfurization approach, it found out that said 3rd object could be attained by contacting the petroleum system hydrocarbon after making a devulcanizing agent contact for a steam-reforming catalyst. This invention is completed based on this knowledge. That is, after carrying out desulfurization processing of the petroleum system hydrocarbon by the desulfurization approach of the petroleum system hydrocarbon characterized by for this invention to desulfurize to (1) support using the devulcanizing agent for petroleum system hydrocarbons and the (2) above-mentioned devulcanizing agent which come to support a basic functional group, and the approach of (3) above (2), the manufacture approach of the hydrogen for fuel cells characterized by to make a steam-reforming catalyst contact offers.

[0008]

[Embodiment of the Invention] First, the devulcanizing agent of this invention is explained. The devulcanizing agent of this invention makes support support a basic functional group. As this support, a porous thing is desirable. As such porosity support, a porosity inorganic oxide, for example, a silica, an alumina, a silica alumina, a zeolite, a titania, a zirconia, a magnesia, a zinc oxide, clay, clay, diatomaceous earth, activated carbon, insoluble synthetic resin, etc. can be mentioned preferably. Although such porosity support may be used independently and you may use combining two or more sorts, in these, insoluble synthetic resin is especially suitable. As insoluble synthetic resin, the synthetic resin which copolymerized and obtained the styrene monomer and the divinylbenzene, the synthetic resin which condensed the meta-phenylenediamine with formaldehyde and obtained it can be used, for example.

[0009] As a basic functional group which such support is made to support, the amino group or the Pori amino group is desirable. Since these functional groups have the strong polarity, the

quality of acidity and a strong polar sulfoxide, or a sulfone is adsorbed easily. As an approach of supporting such a basic functional group to support, the approach by gas adsorption, the approach by the installation from a water solution, the approach by the polymerization reaction of the monomer containing the above-mentioned functional group, etc. are mentioned. Under existence of the gas which contains the amino compound or the Pori amino compounds, such as ammonia and a hydrazine hydrate, as an approach by gas adsorption, for example, There is an approach to which this compound and support are made to react, and as an approach by the installation from a water solution There is an approach by the approach of well-known arbitration, such as an impregnation method using the solution containing the amino compound or the Pori amino compounds, such as ammonia, a hydrazine, a urea, an aniline, and amino alcohol, a coprecipitation method, a method of kneading support gel, and an ion-exchange method. Moreover, the approach of making amines react to what carried out chromium methylation of the copolymer as an approach by the polymerization reaction of the monomer containing the above-mentioned functional group etc. is mentioned.

[0010] The amount of support to the support of the above-mentioned basic functional group has the desirable range per 1g of support, and of 0.1 – 10 milliequivalent. If there is a possibility that the desulfurization engine performance may not fully be demonstrated for this amount of support at less than 0.1 % of the weight and it, on the other hand, exceeds 10 % of the weight, the structure on the support of a basic functional group changes, and it is not desirable. The more desirable amount of support of the field of the desulfurization engine performance to this basic functional group is the range per 1g of support, and of 0.2 – 5 milliequivalent. Moreover, there is especially no limit as a configuration of a devulcanizing agent, for example, the shape of the shape of the letter of grinding, a pellet type, and a tablet and a bead etc. can be mentioned. As a petroleum system hydrocarbon with which the devulcanizing agent of this invention is applied, although LPG, a gasoline, naphtha, kerosene, gas oil, etc. are mentioned for example, the petroleum system hydrocarbon which has the boiling point below kerosene in these is desirable. If it is in kerosene, it is desirable that a sulfur content content applies to the JIS No. 1 kerosene below the 80 weight ppm.

[0011] Next, the desulfurization approach of this invention is explained. After carrying out desulfurization processing of the petroleum system hydrocarbon using the devulcanizing agent of this invention of (1) above-mentioned by the approach (the desulfurization approach I of this invention is called hereafter.) of carrying out desulfurization processing of the petroleum system hydrocarbon, and the (2) above-mentioned desulfurization approach I, there are two modes of an approach (the desulfurization approach II of this invention is called hereafter.) contacted to the second devulcanizing agent in the desulfurization approach of this invention. In the desulfurization approach I of this invention, a petroleum system hydrocarbon can be put into containers, such as an approach of circulating a petroleum system hydrocarbon to a devulcanizing agent, and a tank which fixed the devulcanizing agent to the interior, as a desulfurization format, and standing or the approach of agitating can be mentioned preferably. Moreover, the temperature to which this devulcanizing agent and a petroleum system hydrocarbon are contacted in this case has the desirable range of -40-100 degrees C. Since the adsorption engine performance of a devulcanizing agent will fall if this temperature exceeds 100 degrees C preferably, since the fluidity of this hydrocarbon falls below -40 degrees C, it is not desirable. In addition, a pressure is usually ordinary pressure -1MPa in this case.

[0012] In the above-mentioned desulfurization approach, it is desirable to use the petroleum system hydrocarbon beforehand processed with the oxidizer as a raw material petroleum system hydrocarbon. By such processing, the thiophenes contained in a petroleum system hydrocarbon can oxidize to a sulfoxide compound or a sulfone compound, and the desulfurization engine performance can be made to improve by using the devulcanizing agent of this invention further. As an oxidizer which can be used in this invention, although there is especially no limit, the alkali salt of the alkali salt of a hydrogen peroxide, a peroxy acid, a metal peroxide, and a metal peroxide, a hypochlorous-acid ghost, a chloric-acid ghost, a hypochlorous-acid ghost, or a chloric-acid ghost, ozone, etc. are mentioned preferably. Two or more sorts can be combined and the above-mentioned oxidizer can also be used, although you may use independently. For

oxidizing to a sulfoxide compound or a sulfone compound as amount of the oxidizer used in all the sulfur compounds that are contained in a petroleum system hydrocarbon and that should oxidize, although what is necessary is just more than a complement, it is desirable to usually add 2–8 oxygen atoms per sulfur atom and the oxidizer of the amount which supplies 3–4 oxygen atoms especially, when oxidizing a sulfur compound to a sulfoxide compound or a sulfone compound promptly. Moreover, as for an oxidizer, it is desirable to dissolve and use the handling nature for a petroleum system hydrocarbon and the dissolving solvent from the point made easy.

[0013] In the desulfurization approach II of this invention, after being the above [a petroleum system hydrocarbon], making, using the devulcanizing agent of above-mentioned this invention as the first devulcanizing agent and carrying out desulfurization processing, adsorption desulfurization of this hydrocarbon can be efficiently performed by making the second devulcanizing agent contact. As the second devulcanizing agent of the above, there is especially no limit, it may use another adsorption devulcanizing agent, and may use hydrodesulfurization catalysts, such as Co–Mo/alumina, and a nickel–Mo alumina. As another former adsorption devulcanizing agent, the thing which is chosen, for example from Cr, Mn, Fe, Co, nickel, Cu, Zn, Pd, Ir, and Pt and which supported a kind to porosity support is desirable at least. What supported especially nickel to porosity support is suitable. As for the amount of support of these metal components, it is desirable that it is 30 – 80 % of the weight based on points, such as desulfurization engine performance, to the devulcanizing-agent whole quantity. These adsorption devulcanizing agents can raise the desulfurization engine performance by carrying out hydrogen reduction beforehand. Moreover, in using the latter hydrodesulfurization catalyst, in case it contacts a petroleum system hydrocarbon for this hydrodesulfurization catalyst as the second devulcanizing agent, a small amount of hydrogen may be added.

[0014] It is desirable to contact directly the petroleum system hydrocarbon in which desulfurization processing was carried out by the devulcanizing agent of this invention to the second devulcanizing agent as the desulfurization approach by this second devulcanizing agent. Moreover, beforehand, desulfurization processing is carried out by the devulcanizing agent of this invention, and a petroleum system hydrocarbon may be contacted to the second devulcanizing agent in somewhere else at reaction time. As a reaction condition at the time of making the second devulcanizing agent contact, a petroleum system hydrocarbon can be suitably selected according to the class of the second devulcanizing agent to be used. For example, when a nickel system adsorption devulcanizing agent is used as the second devulcanizing agent and kerosene is used as a petroleum system hydrocarbon, the range of contact temperature is usually 130–230 degrees C, and a pressure is usually ordinary pressure – 1 MPa–G extent. In the desulfurization approach II of such this invention, it is possible by choosing desulfurization conditions suitably to make sulfur content in a petroleum system hydrocarbon below into the 0.2 weight ppm.

[0015] Next, the manufacture approach of the hydrogen for fuel cells of this invention is explained. In this approach, the hydrogen for fuel cells is manufactured by contacting the petroleum system hydrocarbon by which desulfurization processing was carried out in the desulfurization approach of said this invention for a steam-reforming catalyst. As a steam-reforming catalyst used in the approach of this invention, there is especially no limit, out of the well-known thing conventionally known as a steam-reforming catalyst of a hydrocarbon, can choose the thing of arbitration suitably and can use it. As such a steam-reforming catalyst, what supported noble metals, such as nickel, a zirconium or a ruthenium, a rhodium, and platinum, can be mentioned, for example to suitable support. Kind support may be carried out and the above-mentioned support metal may be made to support combining two or more sorts. In these catalysts, the thing (a ruthenium system catalyst is called hereafter.) which made the ruthenium support is desirable, and the effectiveness which controls the carbon deposit under steam-reforming reaction is large. In the case of this ruthenium system catalyst, the amount of support of a ruthenium has 0.05 – 20% of the weight of the desirable range on support criteria, and it is 0.1 – 2% of the weight of the range especially preferably 0.05 to 15% of the weight more preferably.

[0016] When supporting this ruthenium, it can support by request combining other metals. As

these other metals, a zirconium, cobalt, magnesium, etc. are mentioned for example. On the other hand, as support, an inorganic oxide is desirable and an alumina, a silica, a zirconia, magnesia, such mixture, etc. are specifically mentioned. In these, especially an alumina and a zirconia are suitable. a ratio with the carbon which originates in a steam and a petroleum system hydrocarbon as a reaction condition in steam-reforming processing — S/C (mole ratio) — usually — 2-5 — desirable — 2-4 — it is more preferably selected in 2-3. When there is a possibility that the amount of generation of hydrogen may fall [a S/C mole ratio] less than by two and 5 is exceeded, a superfluous steam is needed, a heat loss is large, and since the effectiveness of hydrogen manufacture falls, it is not desirable.

[0017] Moreover, it is desirable to keep the inlet temperature of a steam-reforming catalyst bed at 630 degrees C or less and 600 more degrees C or less, and to perform steam reforming. If inlet temperature exceeds 630 degrees C, the pyrolysis of a hydrocarbon may be promoted, carbon may deposit in a catalyst or a reaction tube wall, and operation may become difficult. In addition, although especially a limit does not have catalyst bed outlet temperature, the range of 650-800 degrees C is desirable. If catalyst bed outlet temperature has fear which is not enough and exceeds 800 degrees C, a reactor may need heat-resisting material and is not economically desirable. reaction pressure — usually — ordinary pressure — 3MPa — desirable — the range of ordinary pressure — 1MPa — it is — moreover, LHSV — usually — 0.1-100h⁻¹ — it is the range of 0.2-50h⁻¹ preferably. Thus, the hydrogen for fuel cells can be manufactured efficiently.

[Translation done.]

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EXAMPLE

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples. In addition, the kerosene used for the desulfurization trial is the JIS No. 1 kerosene of the sulfur content 65 weight ppm. In addition, the distillation curve of the JIS No. 1 kerosene to be used is as follows.

initial boiling point : 152-degree-C 10% distillation-temperature: -- 169-degree-C 30% distillation-temperature: -- 184-degree-C 50% distillation-temperature: -- 203-degree-C 70% distillation-temperature: -- 224-degree-C 90% distillation-temperature: -- 254-degree-C terminal point :

276 degrees C [0019] Copolymerize the preparation styrene monomer and divinylbenzene of an example 1 (1) devulcanizing agent, prepare giant-molecule support (weight average molecular weight 106, a styrene:divinylbenzene ratio: 10:1), and made this giant-molecule support and 90 degrees C of chloro methyl ether react for 2 hours, and added the trimethylamine further, it was made to react at a room temperature for 8 hours, and the devulcanizing agent was obtained. The amount of support of the Pori amino group was 3 milliequivalent per 1g of macromolecule support.

[0020] (2) 2.5l. of desulfurization trial ** JIS No. 1 kerosene was held in the container with a capacity of 5l., 250ml (30%) of hydrogen peroxide solution was added to this, and it stirred at the room temperature for 3 hours. Separation recovery of the part for kerosene was carried out after stirring termination. The sulfur concentration after the recovery obtained by this trial was 50 ppm. After holding 2l. of kerosene obtained by the above-mentioned processing, and 500g of devulcanizing agents obtained by the above (1) in the container with a capacity of 5l. and agitating them at a room temperature for 24 hours, separation recovery of the part for kerosene was carried out. The sulfur content concentration in the collected kerosene was the amount ppm of duplex.

** As the second devulcanizing agent, after calcinating 15ml (70 % of the weight the amount of nickel support : as metal nickel) of nickel support diatomaceous earth at 400 degrees C, the coil made from stainless steel with a bore of 17mm was filled up. Subsequently, after carrying out temperature up to 120 degrees C in the bottom hydrogen air current of ordinary pressure and holding for 1 hour, temperature up was carried out further, it held at 380 degrees C for 1 hour, and the nickel support diatomaceous earth devulcanizing agent was activated. Then, it held at 150 degrees C. Next, the desulfurization kerosene obtained by the aforementioned ** was circulated to the coil in liquid-hourly-space-velocity (LHSV) 10h⁻¹ under ordinary pressure, and the sulfur content concentration in the processing kerosene after 5-hour progress was analyzed. Consequently, sulfur content concentration was below the 0.2 weight ppm.

[0021] The acquired catalyst was dried and the devulcanizing agent was obtained, after adding 680ml of aqueous ammonia 1% to 100g of preparation activated carbon of an example 2 (1) devulcanizing agent. The amount of support of the amino group was 4 milliequivalent per 1g of activated carbon.

(2) When the desulfurization trial was carried out like the example 1 (2) using the devulcanizing agent obtained by the desulfurization test above (1), the sulfur content concentration in the kerosene after 5-hour progress was below the 0.2 weight ppm.

[0022] 250ml (30%) of hydrogen peroxide solution, 50ml of formic acid, and 250ml of acetones

were added to 2.5l. of same IS No. 1 kerosene with having used in example 1 (1) example 1 of a comparison, and 3-hour stirring and a reaction were performed at 40 degrees C. The sodium sulfite water solution of 2 conventions of reaction mixture washes after a reaction, an organic phase is further dried after washing with distilled water, it distills with a precision distillation apparatus, and the fraction of 220-350 degrees C of boiling points is taken. The sulfur content concentration in purification kerosene was 5 % of the weight.

(2) When the desulfurization trial was carried out like example 1 (2) ** using the kerosene obtained by the above (1), the sulfur content concentration in the kerosene after 5-hour progress was the 0.5 weight ppm.

[0023] The kerosene obtained in (1) of the example 1 of example of comparison 2 comparison was diluted with Deccan which does not contain sulfur further, and the sulfur concentration was made into the amount ppm of duplexs. When the desulfurization trial was carried out like example 1 (2) ** using the kerosene diluted with above-mentioned Deccan, the sulfur content concentration in the kerosene after 5-hour progress was the 1.0 weight ppm.

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